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CHEMICAL CHANGES IN CALCIUM ARSENATE DURING STORAGE.

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PURPOSE OF INVESTIGATION.

Soon after calcium arsenate had been introduced into the Cotton Belt for use in the control of the cotton boll weevil, the United States Department of Agriculture began to receive complaints of injury to cotton plants resulting from the application of this material. Chemical analyses showed that much of the calcium arsenate being used in the cotton-growing region at that time contained from 1 to 5 per cent of "water-soluble" arsenic oxid,[2] which explained to some extent the injury that was being done to the plants.

In an endeavor to place the responsibility for this unsatisfactory condition, it was suggested that perhaps commercial calcium arsenates deteriorated somewhat when stored for a period of several weeks or months and that this deterioration was more rapid under the climatic conditions existing in the cotton-growing States. This problem was a very serious one, not only from the standpoint of the consumer but from that of the manufacturer as well, for on its solution depended the answer to the question whether or not it was

[1] L. N. Markovitz and A. Shaver, junior chemists, of the Bureau of Chemistry, assisted in the analytical work, and T. P. Cassidy and M. T. Young, of the Bureau of Entomology, cared for and sampled all the material stored at Tallulah, La.

[2] As determined by the official method of the Association of Official Agricultural Chemists, J. Assn. Offic. Agr. Chemists, 5 (1921): 37.

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safe to use calcium arsenate that had been stored for any appreciable length of time. A preliminary investigation showed that in the cases of the most serious burning reported, the injury was due to the use of improperly made calcium arsenate. The evidence of deterioration seemed sufficiently suggestive, however, to warrant an investigation of the matter under accurately controlled conditions.

RESULTS OF PREVIOUS INVESTIGATIONS.

Robinson[3] showed that chemical changes occur in calcium arsenate through the action of carbon dioxid in the presence of water and stated that under atmospheric conditions a similar but much slower action probably would occur. As a result of bubbling carbon dioxid through suspensions of dicalcium and tricalcium arsenates in water, he concluded that there was an evident "solvent action upon the calcium arsenates." However, while this writer's results for tricalcium arsenate were higher, those for dicalcium arsenate were lower than his figures for the solubility of the same salts in pure water.

Patten and O'Meara[4] suggested that calcium arsenate when applied to foliage would almost certainly be subject to change by the carbon dioxid given off by the leaves. In pursuance of this idea, they determined the amount of arsenic rendered soluble when saturated carbon dioxid water was used in place of distilled water in the regular method for determining water-soluble arsenic oxid in calcium arsenate. The six samples used by them gave an average of 0.7 per cent soluble arsenic oxid with distilled water and an average of 18.5 per cent soluble arsenic oxid with the carbonated water.

The work of the previous investigators was done in connection with the action of carbon dioxid on calcium arsenate when applied to foliage in a thin film and subjected to the effect of moisture. Reedy and Haag,[5] the only workers who have considered the question of a possible change in calcium arsenate during storage, state that "during storage this product undergoes some change in composition which results in a considerable increase in the amount of water-soluble arsenate." They thought at first that moisture and carbon dioxid from the air caused this change, but state that "the use of air-tight containers has not been sufficient to prevent it." However, they report experiments showing that exposure to laboratory air and to moist carbon dioxid caused an increase in the water-soluble arsenic which in the latter case was quite marked. As a result of their work, they conclude that "the decomposition of tricalcium arsenate is due to hydrolysis, which seems to be catalyzed by many substances that

[3] J. Agr. Research, 13 (1918): 288; Oregon Agr. Col. Exp. Sta. Bull. 131 (1918), p. 10.
[4] Mich. Agr. Col. Exp. Sta., Quart. Bull., Nov., 1919, p. 83.
[5] J. Ind. Eng. Chem., 13 (1921): 1038.

may be present as impurities." The results presented are not sufficient to substantiate this conclusion in so far as it applies to deterioration during storage.

RESULTS OF PRESENT INVESTIGATION.

The United States Department of Agriculture recommends the application of calcium arsenate on cotton only in the form of a dust. All of the work here reported, therefore, was done on calcium arsenate in the dry powdered form.

It was realized that if chemical changes occur in calcium arsenate during storage, the type of container in which it is stored, as well as the original composition of the material and the climatic conditions under which it is stored might have an influence on the rate of this change. The plan as outlined therefore was to obtain material representing all of the leading commercial brands on the market and all of the principal types of commercial containers. Two original containers of calcium arsenate from six of the largest manufacturers of this material were stored in a frame warehouse at the Delta Laboratory of the Bureau of Entomology at Tallulah, La. One container of each of these six brands was put in storage intact and disturbed only at stated intervals when samples for analysis were drawn. The material in the other six packages was subdivided, 25-pound portions in each case being put into various standard types of containers and the remaining material, from 50 to 100 pounds, retained in the original container. Four other samples, three of which represented brands included in the six just mentioned, were placed in storage in the building occupied by the Insecticide and Fungicide Board (220 Thirteenth Street SW, Washington, D. C.). These were not subdivided. Samples were drawn at intervals from all of these containers for analysis.[6]

The following scheme of marking for the identification of the various brands of calcium arsenate, the place of storage, and the kind of container, was adopted: Brands or manufacturers, *A*, *B*, *C*, *F*, *H*, *I*, and *J;* material stored in Washington, *W*, immediately after the letter designating the manufacturer; material stored in Tallulah, in original containers and without subdivision, *T;* sets that were subdivided and used for the container tests, *S*. All subdivisions were stored at Tallulah.

COMPOSITION OF ORIGINAL SAMPLES.

The results of the analyses of the samples made at the time of collection are given in Table 1.

[6] In sampling the material was disturbed as little as possible. Several cores were taken by means of a trier, about 1¼ inches in diameter, at various places and extending at different angles from the top of the package to the bottom. The head of the container was immediately replaced, or the holes through which the trier was inserted were tightly closed.

TABLE 1.—*Composition of calcium arsenates at the beginning of the period of storage.*

Sample.	Arsenic oxid (As_2O_5).	Calcium oxid (CaO).	Magnesium oxid (MgO).	Lead oxid (PbO).	Copper oxid (CuO).	Oxids of iron and aluminum (R_2O_3).	Antimonic oxid (Sb_2O_5).	Acid-insoluble material.	Loss on ignition.	Total.	Carbon dioxid (CO_2).	Water-soluble arsenic oxid (As_2O_5).
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
AT	40.55	43.16	1.82	Trace.	.....	0.44	0.02	0.45	10.88	97.32	2.31	0.02
AS	40.18	39.76	1.88	0.91	.....	2.51	.05	.44	10.24	95.97	2.78	.08
AW	42.95	42.76	1.41	Trace.	.....	.40	.07	.16	8.96	96.71	1.78	.08
BT	41.12	40.57	1.34	Trace.	.....	.66	.16	.23	13.90	97.98	3.62	.20
BS	40.81	38.96	1.78	0.70	0.70	2.10	.19	.57	11.40	97.21	5.30	.35
BW	40.58	39.89	2.08	Trace.	.....	1.12	.21	.62	11.85	96.35	3.44	.69
CT	39.35	36.92	.22	9.48	.....	.52	.53	.24	8.85	96.11	3.30	.83
CS	41.59	43.06	.38	.77	.....	.38	.50	.44	8.99	96.11	4.47	.15
FT	44.10	43.80	.48	.63	.....	1.42	.14	.62	4.88	96.07	1.40	.00
FS	45.07	42.87	.32	.77	.....	1.41	.21	.45	5.05	96.15	1.91	.03
HT	41.58	41.04	.82	.72	.....	2.22	.11	1.08	6.72	94.29	1.33	.10
HS	42.37	42.05	1.33	.70	.....	1.54	.11	1.00	6.33	95.43	1.07	.10
HW	43.10	40.35	3.37	.28	.....	2.08	.07	1.09	6.86	97.20	.91	.11
IT	40.91	43.16	.75	1.36	.....	1.50	.08	.71	8.05	96.52	5.95	.08
IS	44.40	43.16	.53	.73	.....	.86	.19	.77	6.08	96.72	5.69	.39
JW	45.65	40.55	1.18	.32	.....	.92	.29	.32	5.37	94.60	2.69	.30

It will be noted that the arsenic oxid content exceeds 40 per cent in every case, except that of the sample containing lead, and that the calcium oxid and arsenic oxid values are approximately equal. This is as it should be in a properly made calcium arsenate to be used for insecticidal purposes. The impurities are low in all cases except one, sample *CT*, which contains more than 9 per cent of lead expressed as the oxid. This is probably present in the form of lead arsenate as a result of carelessness in manufacture. The presence of small quantities of lead in the other samples is doubtless caused by the use in their manufacture of apparatus that had previously been employed in making lead arsenate. The copper in sample *BS* apparently owed its origin to the presence of Bordeaux mixture, as small pieces of a blue material resembling this product were visible. The water-soluble arsenic oxid figures are reasonably low in all cases except two, one of which is the sample containing an appreciable quantity of lead.

CARBON DIOXID AND WATER-SOLUBLE ARSENIC OXID IN STORED SAMPLES.

The chemical criterion employed in the estimation of deterioration in calcium arsenate is the change in the so-called water-soluble arsenic oxid. All of the work quoted from the literature showed that contact with carbon dioxid in the presence of water may greatly increase the content of soluble arsenic oxid. The authors' experience accords with this. When carbon dioxid is bubbled through an aqueous suspension of commercial calcium arsenate for a sufficient length of time, the quantity of arsenic oxid rendered soluble is approximately the same as that obtained when dicalcium arsenate is treated with water alone, in the same concentration. Further, calcium carbonate, under ordinary conditions, neutralizes arsenic acid only to the dicalcium arsenate stage, showing that a basic mixture tends to revert, by

the absorption of carbon dioxid, to a mixture of calcium carbonate and dicalcium arsenate. It appeared that any increase in water-soluble arsenic oxid in commercial calcium arsenate during storage, therefore, would probably be the result of absorption of carbon dioxid from the air.

Accordingly, the authors decided to determine both carbon dioxid and water-soluble arsenic oxid in all of the samples and subdivisions at successive intervals. Soluble arsenic oxid was determined by the official method of the Association of Official Agricultural Chemists and carbon dioxid in a specially designed apparatus similar to that described by W. H. Chapin.[7] This method did not give extremely accurate results but it is very rapid and sufficiently accurate for this work. Duplicate determinations seldom differed by more than 0.10 per cent. The fact that the results here vary more than this from the curves drawn may be explained on the basis of uneven distribution of the material in the barrels and the method of sampling. The subsamples were always thoroughly mixed, but they were taken from the barrels by means of a trier, and, since carbon dioxid must work its way through from the outside of the package, it is reasonable to suppose that three or four trierfulls might not always remove a strictly representative sample. Taken as a whole, however, the results leave no doubt of the fact that carbon dioxid is absorbed under certain conditions.

The results of these examinations are reported in Table 2 and are also shown graphically in Figures 1 to 46. The results on all the samples obtained from one manufacturer are presented before those of another are shown. Within each of these groups the order is as follows: Unsubdivided sample kept at Washington; unsubdivided sample kept at Tallulah; portion of subdivided sample kept at Tallulah in original container; subdivided samples at Tallulah representing the different container tests. The last subdivisions are indicated by figures following the letter designation as follows: 1, sheet-iron drum; 2, unlined sugar barrel; 3, paper-lined sugar barrel; 4, heavy hardwood barrel; 5, unlined veneer drum; 6, paper-lined veneer drum.

In every graph the arsenic oxid values are represented by a solid line and the carbon dioxid values by a broken line. The curves are drawn in what seemed to be the most probable positions without attempting to calculate them. In order to bring out more clearly the relationship between their variations, the ordinate scale of arsenic oxid (As_2O_5) values has been magnified to five times that of the carbon dioxid (CO_2) values. The horizontal spaces on all the plots indicate intervals of three months, the initial ordinate representing in each case December 1, 1919.

[7] J. Ind. Eng. Chem., 10 (1918): 527.

TABLE 2.—*Effect of storage on chemical composition of calcium arsenate.*

Sample examined.	Date sampled.	Period of storage.	Water-soluble arsenic oxid (As_2O_5).	Carbon dioxid (CO_2).
AW (100 pounds in hardwood barrel)	1920.	*Mos.*	*Per ct.*	*Per ct.*
	Apr. 12	.....	0.08	1.78
	June 23	2.4	.07	1.88
	1921.			
	Jan. 14	9.1	.07	1.90
	July 20	15.3	.10	1.84
	Nov. 25	19.4	.08	1.92
	1922.			
	Mar. 1	22.6	.08	.....
AT (200 pounds in hardwood barrel)	1919.			
	Dec. 1	.....	.02	2.38
	1920.			
	Jan. 8	1.2	.05	2.35
	Feb. 6	2.2	.05	2.36
	Mar. 6	3.2	.02	2.41
	Apr. 7	4.2	.03	2.41
	May 4	5.1	.05	2.46
	June 10	6.3	.04	2.70
	July 14	7.4	.05	2.84
	Aug. 14	8.4	.05	2.99
	Sept. 17	9.5	.05	2.55
	Oct. 15	10.5	.06	2.58
	Nov. 17	11.5	.05	3.18
	Dec. 15	12.5	.06	3.28
	1921.			
	Jan. 15	13.5	.05	3.52
	Apr. 2	16.0	.04	3.11
	July 1	19.0	.08	4.12
	Oct. 1	22.0	.17	4.88
	1922.			
	Jan. 2	25.0	.10	3.55
AS (50 pounds in hardwood barrel)	1920.			
	Apr. 20	.....	.08	2.78
	June 10	1.7	.02	2.53
	July 14	2.8	.03	2.72
	Aug. 14	3.8	.02	2.64
	Sept. 17	4.9	.04	2.65
	Oct. 15	5.8	.02	2.72
	Nov. 17	6.9	.02	2.64
	Dec. 15	7.8	.05	3.26
	1921.			
	Jan. 15	8.8	.05	3.13
	Apr. 2	11.4	.06	3.42
	July 1	14.3	.09	4.64
	Oct. 1	17.3	.07	4.53
	1922.			
	Jan. 2	20.4	.15	5.30
AS-1 (25 pounds in metal drum)	1920.			
	Apr. 20	.....	.07	2.92
	June 10	1.7	.03	2.85
	July 14	2.8	.03	2.50
	Aug. 14	3.8	.02	2.47
	Sept. 17	4.9	.02	2.46
	Oct. 15	5.8	.02	2.62
	Nov. 17	6.9	.02	2.53
	Dec. 15	7.8	.04	2.76
	1921.			
	Jan. 15	8.8	.05	2.83
	Apr. 2	11.4	.05	2.78
	July 1	14.3	.05	2.60
	Oct. 1	17.3	.05	2.52
	1922.			
	Jan. 2	20.4	.04	2.58
AS-2 (25 pounds in unlined sugar barrel)	1920.			
	Apr. 20	.....	0.06	2.94
	June 10	1.7	.03	3.04
	July 14	2.8	.05	3.85
	Aug. 14	3.8	.04	4.11
	Sept. 17	4.9	.07	4.41
	Oct. 15	5.8	.07	4.94
	Nov. 17	6.9	.13	4.97
	Dec. 15	7.8	.17	5.50
	1921.			
	Jan. 15	8.8	.17	5.57
	Apr. 2	11.4	.25	5.81
	July 1	14.3	.30	6.23
	Oct. 1	17.3	.33	6.08
	1922.			
	Jan. 2	20.4	.35	6.20
AS-3 (25 pounds in paper-lined sugar barrel)	1920.			
	Apr. 20	.....	.05	2.93
	June 10	1.7	.05	3.56
	July 14	2.8	.04	3.27
	Aug. 14	3.8	.05	4.22
	Sept. 17	4.9	.07	4.51
	Oct. 15	5.8	.05	4.04
	Nov. 17	6.9	.24	5.74
	Dec. 15	7.8	.20	5.65
	1921.			
	Jan. 15	8.8	.25	5.80
	Apr. 2	11.4	.34	6.03
	July 1	14.3	.30	6.04
	Oct. 1	17.3	.33	6.15
	1922.			
	Jan. 2	20.4	.37	6.24
AS-4 (25 pounds in hardwood barrel)	1920.			
	Apr. 20	.....	.05	2.83
	June 10	1.7	.06	3.15
	July 14	2.8	.07	4.18
	Aug. 14	3.8	.07	4.82
	Sept. 17	4.9	.26	5.83
	Oct. 15	5.8	.37	6.18
	Nov. 17	6.9	.38	6.14
	Dec. 15	7.8	.38	6.22
	1921.			
	Jan. 15	8.8	.37	6.02
	Apr. 2	11.4	.36	6.10
	July 1	14.3	.39	6.22
	Oct. 1	17.3	.42	6.18
	1922.			
	Jan. 2	20.4	.44	6.49
AS-5 (25 pounds in unlined veneer drum)	1920.			
	Apr. 20	.....	.05	3.01
	June 10	1.7	.03	2.87
	July 14	2.8	.04	3.19
	Aug. 14	3.8	.05	3.66
	Sept. 17	4.9	.05	3.68
	Oct. 15	5.8	.02	3.64
	Nov. 17	6.9	.05	3.95
	Dec. 15	7.8	.07	4.59
	1921.			
	Jan. 15	8.8	.12	5.04
	Apr. 2	11.4	.19	5.28
	July 1	14.3	.20	5.78
	Oct. 1	17.3	.31	5.86
	1922.			
	Jan. 2	20.4	.35	6.03

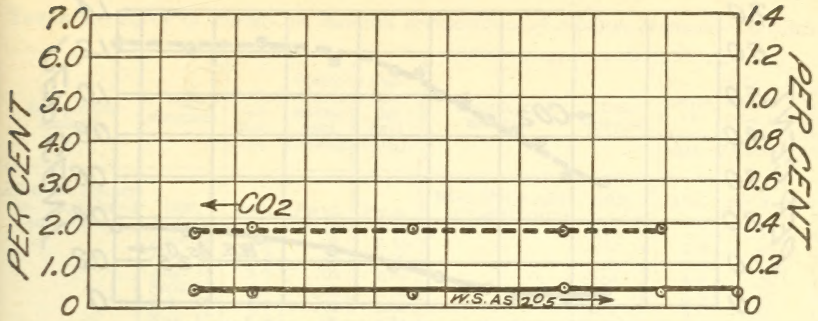

FIG. 1.—Sample AW (100 pounds in hardwood barrel).

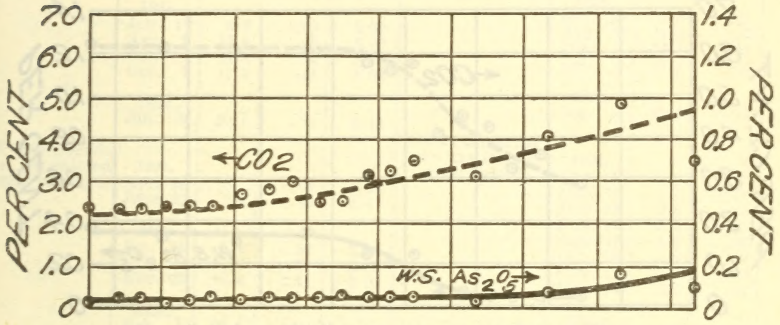

FIG. 2.—Sample AT (200 pounds in hardwood barrel).

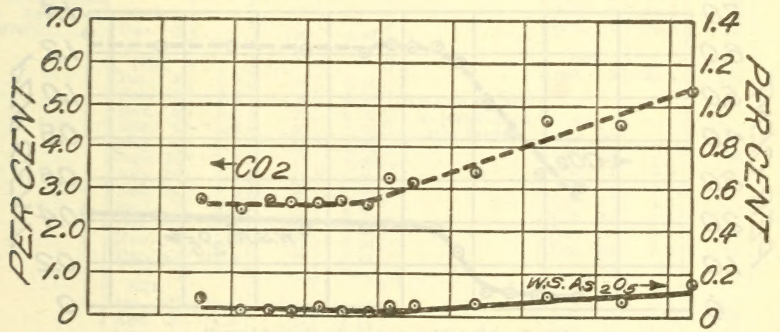

FIG. 3.—Sample AS (50 pounds in hardwood barrel).

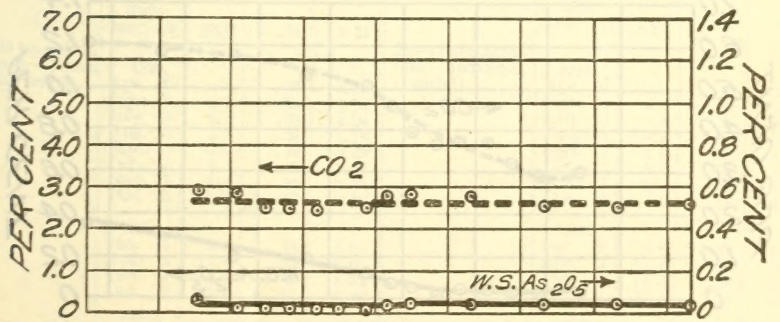

FIG. 4.—AS-1 (25 pounds in metal drum).

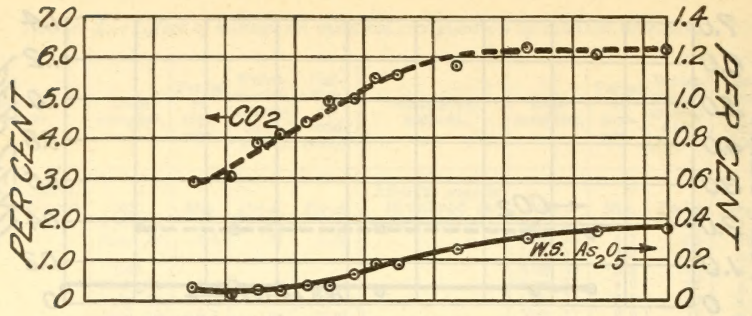

FIG. 5.—AS-2 (25 pounds in unlined sugar barrel).

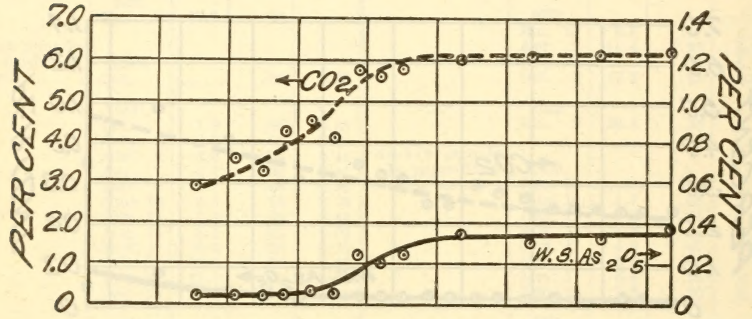

FIG. 6.—AS-3 (25 pounds in paper-lined sugar barrel).

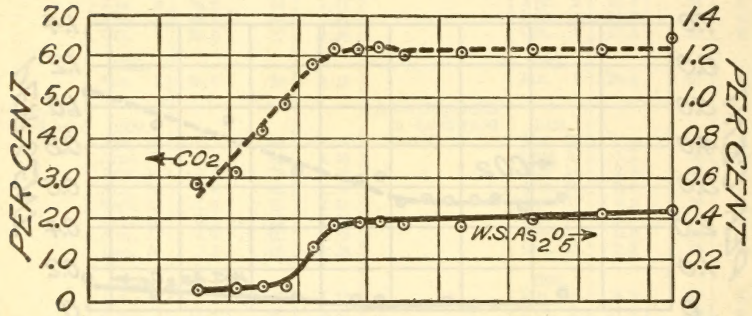

FIG. 7.—AS-4 (25 pounds in hardwood barrel).

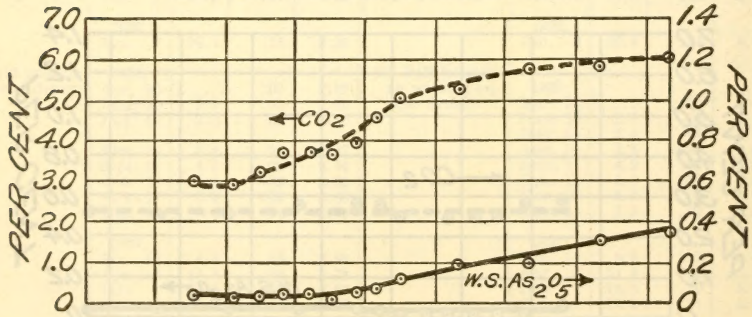

FIG. 8.—AS-5 (25 pounds in unlined veneer drum).

TABLE 2.—*Effect of storage on chemical composition of calcium arsenate*—Continued.

Sample examined.	Date sampled.	Period of storage.	Water-soluble arsenic oxid (As_2O_5).	Carbon dioxid (CO_2).
AS-6 (25 pounds in paper-lined veneer drum)...	1920.	*Mos.*	*Per ct.*	*Per ct.*
	Apr. 20	.....	0.05	2.86
	June 10	1.7	.03	2.85
	July 14	2.8	.04	2.67
	Aug. 14	3.8	.05	2.88
	Sept. 17	4.9	.02	3.08
	Oct. 15	5.8	.02	2.80
	Nov. 17	6.9	.05	3.64
	Dec. 15	7.8	.06	3.47
	1921.			
	Jan. 15	8.8	.08	3.92
	Apr. 2	11.4	.05	4.00
	July 1	14.3	.12	5.38
	Oct. 1	17.3	.13	5.02
	1922.			
	Jan. 2	20.4	.23	5.58
BW (100 pounds in paper-lined sugar barrel)...	1920.			
	Apr. 12	.....	.69	3.44
	June 23	2.4	.46	3.47
	1921.			
	Jan. 14	9.1	.82	3.63
	July 20	15.3	.71	3.86
	Nov. 26	19.4	1.11	4.01
	1922.			
	May 1	22.6	1.09	.....
BT (100 pounds in hardwood barrel).....	1919.			
	Dec. 1	.....	.20	3.62
	1920.			
	Jan. 8	1.2	.23	3.68
	Feb. 6	2.2	.22	3.68
	Mar. 6	3.2	.27	3.70
	Apr. 7	4.2	.30	3.76
	May 4	5.1	.16	3.70
	June 10	6.3	.19	3.98
	July 14	7.4	.18	4.01
	Aug. 14	8.4	.17	3.82
	Sept. 17	9.5	.17	3.80
	Oct. 15	10.5	.22	4.28
	Nov. 17	11.5	.27	4.36
	Dec. 15	12.5	.27	4.82
	1921.			
	Jan. 15	13.5	.27	4.70
	Apr. 2	16.0	.20	4.14
	July 1	19.0	.28	4.68
	Oct. 1	22.0	.33	4.74
	1922.			
	Jan. 2	25.0	.31	4.72
BS (50 pounds in paper-lined sugar barrel)...	1920.			
	Apr. 20	.....	.35	5.30
	June 10	1.7	.25	4.93
	July 14	2.8	.28	4.84
	Aug. 14	3.8	.26	5.19
	Sept. 17	4.9	.40	5.28
	Oct. 15	5.8	.32	5.42
	Nov. 17	6.9	.55	6.06
	Dec. 15	7.8	.47	6.00
	1921.			
	Jan. 15	8.8	.48	5.97
	Apr. 2	11.4	.52	6.01
	July 1	14.3	.62	6.69
	Oct. 1	17.3	.71	6.69
	1922.			
	Jan. 2	20.4	.76	7.00
BS-1 (25 pounds in metal drum)	1920.			
	Apr. 20	.....	0.35	5.12
	June 10	1.7	.24	4.72
	July 14	2.8	.20	4.53
	Aug. 14	3.8	.17	4.74
	Sept. 17	4.9	.24	4.49
	Oct. 15	5.8	.20	4.46
	Nov. 17	6.9	.22	4.61
	Dec. 15	7.8	.20	4.8.
	1921.			
	Jan. 15	8.8	.21	5.00
	Apr. 2	11.4	.25	4.74
	July 1	14.3	.18	4.64
	Oct. 1	17.3	.19	4.43
	1922.			
	Jan. 2	20.4	.17	4.54
BS-2 (25 pounds in unlined sugar barrel)...	1920.			
	Apr. 20	.....	.30	5.19
	June 10	1.7	.37	5.30
	July 14	2.8	.35	5.44
	Aug. 14	3.8	.53	6.26
	Sept. 17	4.9	.67	6.10
	Oct. 15	5.8	.69	6.64
	Nov. 17	6.9	.79	6.96
	Dec. 15	7.8	.74	7.05
	1921.			
	Jan. 15	8.8	.77	7.06
	Apr. 2	11.4	.82	7.09
	July 1	14.3	.76	7.25
	Oct. 1	17.3	.78	6.90
	1922.			
	Jan. 2	20.4	.87	7.05
BS-3 (25 pounds in paper-lined sugar barrel)...	1920.			
	Apr. 20	.....	.32	5.12
	June 10	1.7	.46	5.61
	July 14	2.8	.60	6.06
	Aug. 14	3.8	.62	6.46
	Sept. 17	4.9	.75	6.61
	Oct. 15	5.8	.72	6.68
	Nov. 17	6.9	.77	6.95
	Dec. 15	7.8	.74	7.13
	1921.			
	Jan. 15	8.8	.77	7.15
	Apr. 2	11.4	.76	7.01
	July 1	14.3	.76	7.05
	Oct. 1	17.3	.76	7.20
	1922.			
	Jan. 2	20.4	.85	7.00
BS-4 (25 pounds in hardwood barrel).....	1920.			
	Apr. 20	.....	.29	4.87
	June 10	1.7	.27	4.59
	July 14	2.8	.25	4.56
	Aug. 14	3.8	.25	4.78
	Sept. 17	4.9	.25	4.32
	Oct. 15	5.8	.22	4.46
	Nov. 17	6.9	.30	5.16
	Dec. 15	7.8	.29	4.89
	1921.			
	Jan. 15	8.8	.32	5.05
	Apr. 2	11.4	.30	5.08
	July 1	14.3	.30	5.35
	Oct. 1	17.3	.59	6.66
	1922.			
	Jan. 2	20.4	.68	6.51

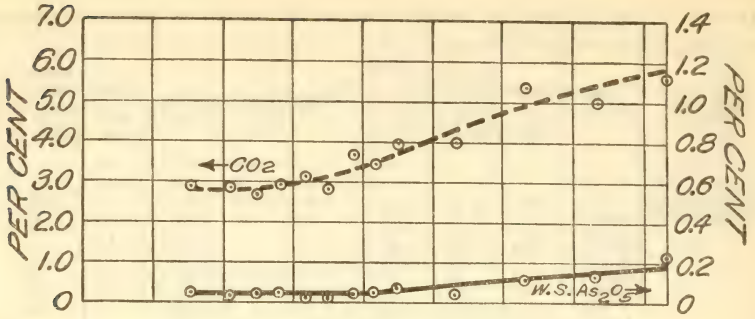

FIG. 9.—AS-6 (25 pounds in paper-lined veneer drum).

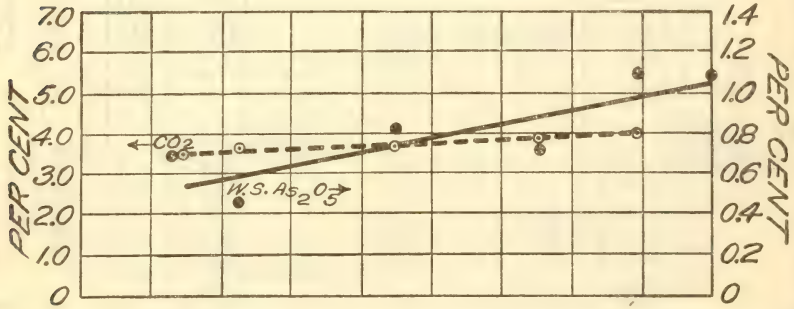

FIG. 10.—BW (100 pounds in paper-lined sugar barrel).

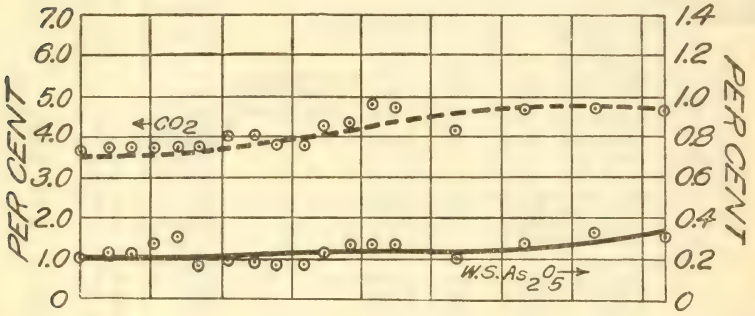

FIG. 11.—BT (100 pounds in hardwood barrel).

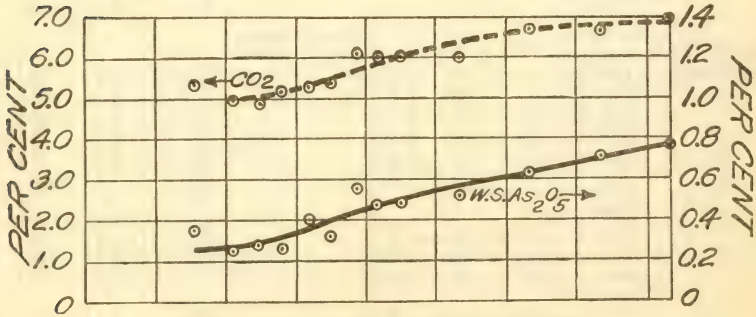

FIG. 12.—BS (50 pounds in paper-lined sugar barrel).

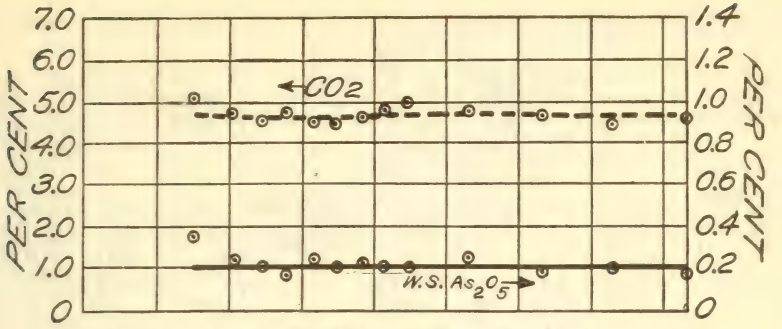

FIG. 13.—BS-1 (25 pounds in metal drum).

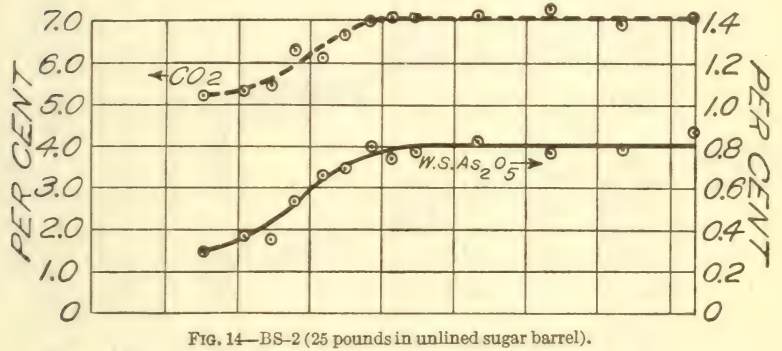

FIG. 14—BS-2 (25 pounds in unlined sugar barrel).

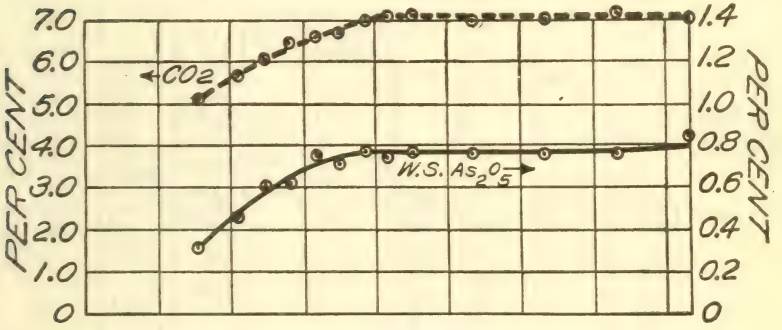

FIG. 15.—BS-3 (25 pounds in paper-lined sugar barrel).

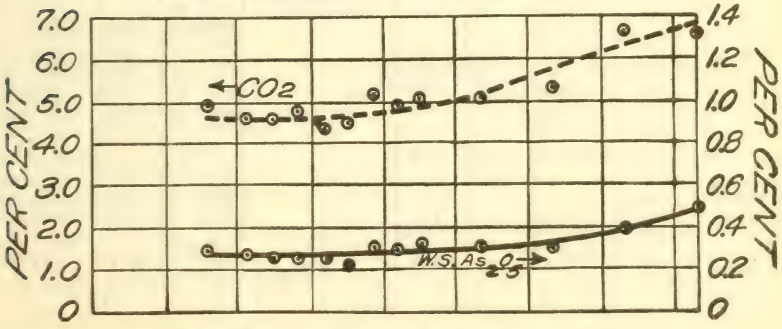

FIG. 16.—BS-4 (25 pounds in hardwood barrel).

TABLE 2.—*Effect of storage on chemical composition of calcium arsenate*—Continued.

Sample examined.	Date sampled.	Period of storage.	Water-soluble arsenic oxid (As_2O_5).	Carbon di-oxid (CO_2).
BS-5 (25 pounds in unlined veneer drum)..	1920.	*Mos.*	*Per ct.*	*Per ct.*
	Apr. 20	.....	0.29	4.80
	June 10	1.7	.35	5.15
	July 14	2.8	.30	5.08
	Aug. 14	3.8	.36	5.68
	Sept. 17	4.9	.50	5.80
	Oct. 15	5.8	.48	5.88
	Nov. 17	6.9	.69	.....
	Dec. 15	7.8	.67	6.63
	1921.			
	Jan. 15	8.8	.64	6.84
	Apr. 2	11.4	.74	7.11
	July 1	14.3	.73	7.23
	Oct. 1	17.3	.76	6.97
	1922.			
	Jan. 2	20.4	.94	7.07
BS-6 (25 pounds in paper-lined veneer drum)..	1920.			
	Apr. 20	.....	.34	4.79
	June 10	1.7	.27	4.74
	July 14	2.8	.28	4.83
	Aug. 14	3.8	.25	5.28
	Sept. 17	4.9	.42	5.10
	Oct. 15	5.8	.32	5.11
	Nov. 17	6.9	.39	.....
	Dec. 15	7.8	.43	5.93
	1921.			
	Jan. 15	8.8	.55	6.23
	Apr. 2	11.4	.60	6.68
	July 1	14.3	.67	6.91
	Oct. 1	17.3	.72	6.93
	1922.			
	Jan. 2	20.4	.94	6.99
CT (100 pounds in paper-lined veneer drum)..	1919.			
	Dec. 1	.....	.83	3.30
	1920.			
	Jan. 8	1.2	.76	3.29
	Feb. 6	2.2	.65	3.33
	Mar. 6	3.2	.56	3.45
	Apr. 7	4.2	.44	3.52
	May 4	5.1	.52	3.60
	June 10	6.3	.54	3.74
	July 14	7.4	.60	3.79
	Aug. 14	8.4	.69	3.90
	Sept. 17	9.5	.47	3.43
	Oct. 15	10.5	.52	3.63
	Nov. 17	11.5	.69	3.87
	Dec. 15	12.5	.63	4.19
	1921.			
	Jan. 15	13.5	.55	3.93
	Apr. 2	16.0	.43	5.97
	July 1	19.0	.62	3.98
	Oct. 1	22.0	.71	4.17
	1922.			
	Jan. 2	25.0	.70	4.40
CS (50 pounds in paper-lined veneer drum)....	1920.			
	Apr. 20	.....	.15	4.47
	June 10	1.7	.18	4.42
	July 14	2.8	.18	4.76
	Aug. 14	3.8	.24	5.24
CS (50 pounds in paper-lined veneer drum) (continued.)	Sept. 17	4.9	0.36	4.89
	Oct. 15	5.8	.35	5.47
	Nov. 17	6.9	.40	5.78
	Dec. 15	7.8	.38	5.61
	1921.			
	Jan. 15	8.8	.41	5.78
	Apr. 2	11.4	.64	4.04
	July 1	14.3	.41	6.18
	Oct. 1	17.3	.45	5.90
	1922.			
	Jan. 2	20.4	.54	6.22
CS-1 (25 pounds in metal drum)	1920.			
	Apr. 20	.....	.15	4.68
	June 10	1.7	.14	4.33
	July 14	2.8	.14	4.22
	Aug. 14	3.8	.14	4.63
	Sept. 17	4.9	.17	4.37
	Oct. 15	5.8	.11	4.31
	Nov. 17	6.9	.12	4.47
	Dec. 15	7.8	.12	4.10
	1921.			
	Jan. 15	8.8	.13	4.60
	Apr. 2	11.4	.14	4.22
	July 1	14.3	.14	4.59
	Oct. 1	17.3	.14	4.38
	1922.			
	Jan. 2	20.4	.12	4.20
CS-2 (25 pounds in unlined sugar barrel).....	1920.			
	Apr. 20	.....	.14	4.47
	June 10	1.7	.20	4.88
	July 14	2.8	.27	5.31
	Aug. 14	3.8	.36	5.22
	Sept. 17	4.9	.47	5.78
	Oct. 15	5.8	.43	5.73
	Nov. 17	6.9	.47	6.15
	Dec. 15	7.8	.47	6.00
	1921.			
	Jan. 15	8.8	.45	6.30
	Apr. 2	11.4	.42	6.17
	July 1	14.3	.44	6.25
	Oct. 1	17.3	.42	6.00
	1922.			
	Jan. 2	20.4	.54	6.20
CS-3 (25 pounds in paper-lined sugar barrel)..	1920.			
	Apr. 20	.....	.15	4.40
	June 10	1.7	.16	4.47
	July 14	2.8	.17	4.86
	Aug. 14	3.8	.38	5.71
	Sept. 17	4.9	.50	5.98
	Oct. 15	5.8	.45	5.76
	Nov. 17	6.9	.46	6.06
	Dec. 15	7.8	.43	6.14
	1921.			
	Jan. 15	8.8	.46	6.04
	Apr. 2	11.4	.42	6.14
	July 1	14.3	.44	6.31
	Oct. 1	17.3	.44	6.31
	1922.			
	Jan. 2	20.4	.52	6.26

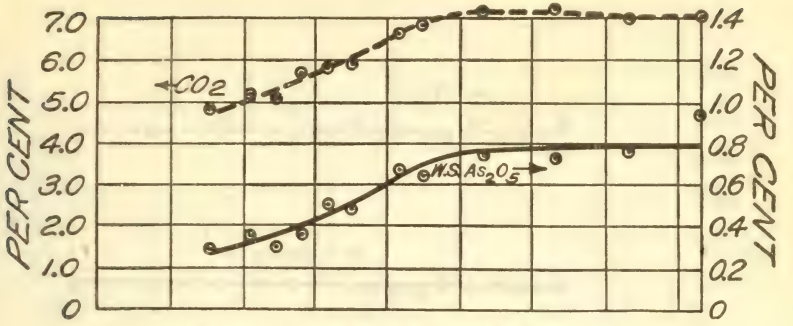

FIG. 17.—BS-5 (25 pounds in unlined veneer drum).

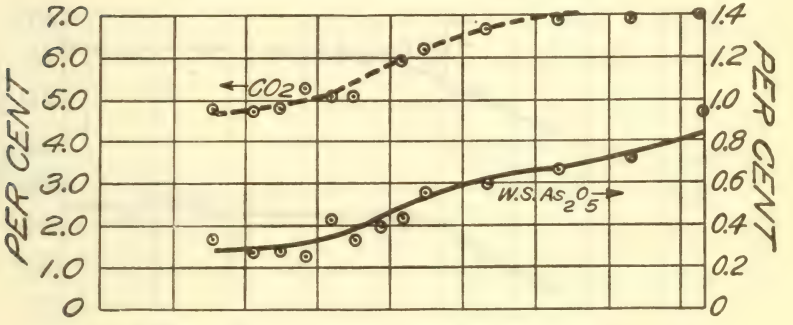

FIG. 18.—BS-6 (25 pounds in paper-lined veneer drum).

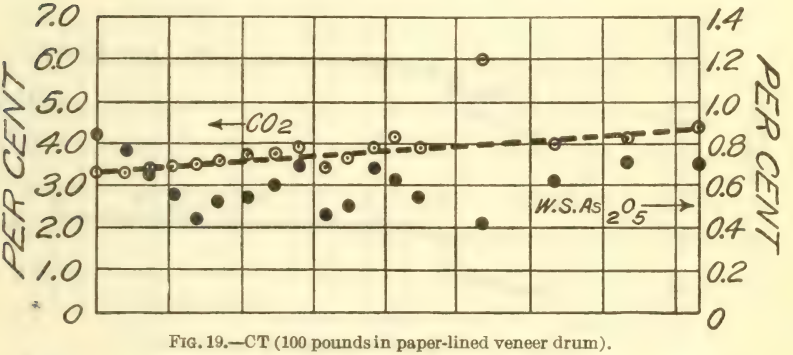

FIG. 19.—CT (100 pounds in paper-lined veneer drum).

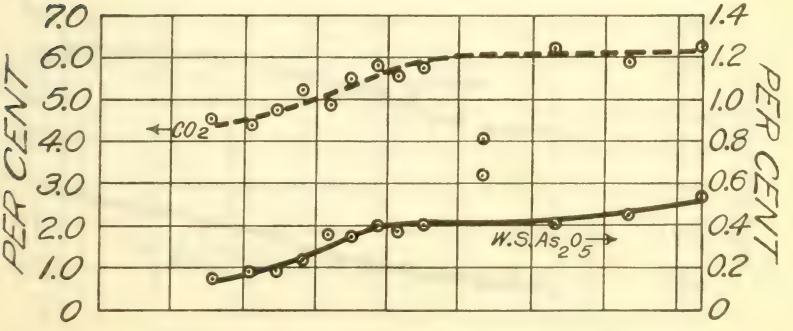

FIG. 20.—CS (50 pounds in paper-lined veneer drum).

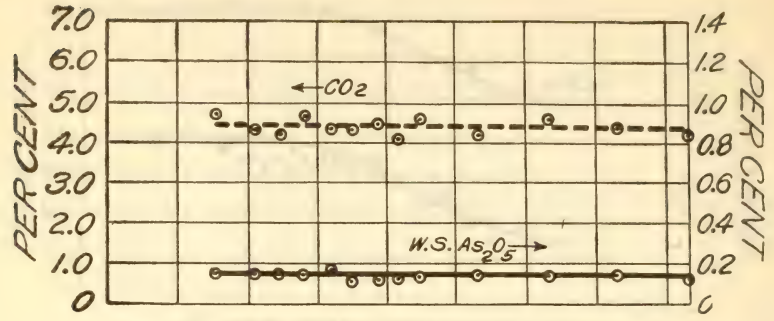

FIG. 21.—CS-1 (25 pounds in metal drum).

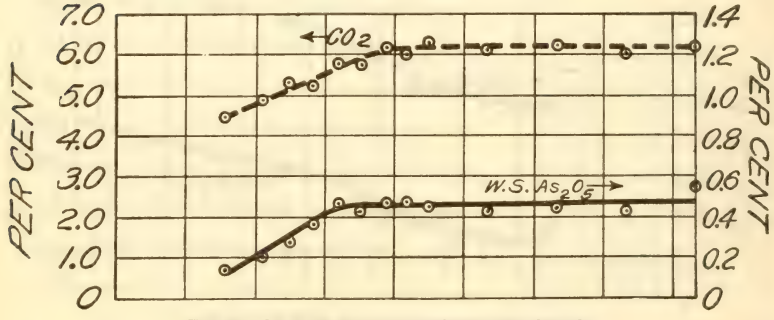

FIG. 22.—CS-2 (25 pounds in unlined sugar barrel).

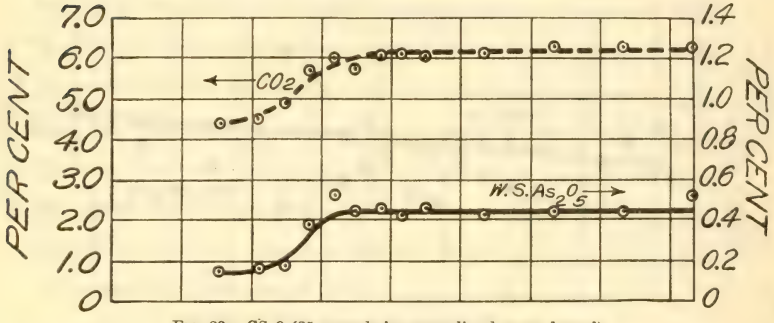

FIG. 23.—CS-3 (25 pounds in paper-lined sugar barrel).

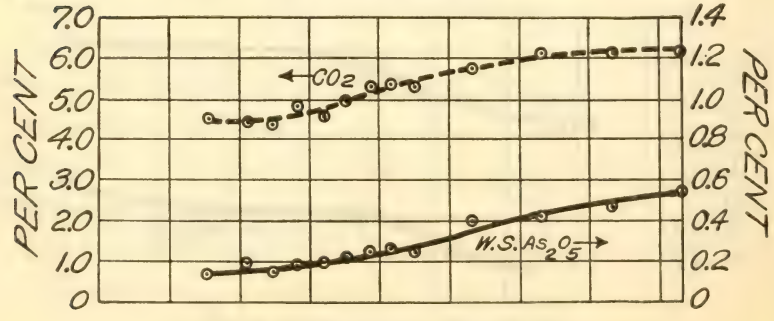

FIG. 24.—CS-4 (25 pounds in hardwood barrel).

TABLE 2.—*Effect of storage on chemical composition of calcium arsenate*—Continued.

Sample examined.	Date sampled.	Period of storage.	Water-soluble arsenic oxid (As_2O_5).	Carbon di-oxid (CO_2).
	1920.	*Mos.*	*Per ct.*	*Per ct.*
CS-4 (25 pounds in hardwood barrel)	Apr. 20	.....	0.14	4.54
	June 10	1.7	.19	4.45
	July 14	2.8	.15	4.37
	Aug. 14	3.8	.18	4.84
	Sept. 17	4.9	.20	4.57
	Oct. 15	5.8	.22	4.92
	Nov. 17	6.9	.25	5.33
	Dec. 15	7.8	.27	5.36
	1921.			
	Jan. 15	8.8	.25	5.32
	Apr. 2	11.4	.40	5.75
	July 1	14.3	.42	6.09
	Oct. 1	17.3	.47	6.14
	1922.			
	Jan. 2	20.4	.54	6.08
	1920.			
CS-5 (25 pounds in unlined veneer drum)	Apr. 20	.....	.17	4.91
	June 10	1.7	.16	4.51
	July 14	2.8	.20	4.54
	Aug. 14	3.8	.17	4.94
	Sept. 17	4.9	.34	5.40
	Oct. 15	5.8	.37	5.67
	Nov. 17	6.9	.45	5.72
	Dec. 15	7.8	.46	6.28
	1921.			
	Jan. 15	8.8	.46	6.36
	Apr. 2	11.4	.46	6.06
	July 1	14.3	.45	6.24
	Oct. 1	17.3	.43	6.07
	1922.			
	Jan. 2	20.4	.51	6.91
	1920.			
CS-6 (25 pounds in paper-lined veneer drum)	Apr. 20	.....	.15	4.80
	June 10	1.7	.16	4.24
	July 14	2.8	.16	4.24
	Aug. 14	3.8	.17	4.62
	Sept. 17	4.9	.20	4.39
	Oct. 15	5.8	.13	4.56
	Nov. 17	6.9	.24	5.06
	Dec. 15	7.8	.20	5.44
	1921.			
	Jan. 15	8.8	.25	5.30
	Apr. 2	11.4	.20	5.29
	July 1	14.3	.39	5.59
	Oct. 1	17.3	.48	5.91
	1922.			
	Jan. 2	20.4	.54	5.83
	1920.			
FT (100 pounds in unlined veneer drum)	Apr. 7	.....	.00	1.40
	May 4	.9	.01	1.44
	June 10	2.1	.03	1.62
	July 14	3.2	.03	1.65
	Aug. 14	4.2	.03	1.66
	Sept. 17	5.3	.02	1.83
	Oct. 15	6.3	.02	1.94
	Nov. 17	7.3	.02	2.79
	Dec. 15	8.3	.02	2.38
	1921.			
	Jan. 15	9.3	.02	2.41
	Apr. 2	11.8	.02	2.52
	July 1	14.7	.05	3.97
	Oct. 1	17.8	.04	3.78
	1922.			
	Jan. 2	20.8	.09	3.09
	1920.			
FS (75 pounds in paper-lined veneer drum)	Apr. 20	.....	0.04	1.91
	June 10	1.7	.06	1.85
	July 14	2.8	.06	2.94
	Aug. 14	3.8	.07	3.62
	Sept. 17	4.9	.07	2.75
	Oct. 15	5.8	.05	3.36
	Nov. 17	6.9	.10	4.81
	Dec. 15	7.8	.07	4.30
	1921.			
	Jan. 15	8.8	.10	4.19
	Apr. 2	11.4	.11	4.26
	July 1	14.3	.22	5.54
	Oct. 1	17.3	.26	5.28
	1922.			
	Jan. 2	20.4	.36	5.75
	1920.			
FS-1 (25 pounds in metal drum)	Apr. 20	.....	.05	2.09
	June 10	1.7	.05	1.72
	July 14	2.8	.03	1.64
	Aug. 14	3.8	.05	1.74
	Sept. 17	4.9	.05	1.67
	Oct. 15	5.8	.05	1.88
	Nov. 17	6.9	.05	1.70
	Dec. 15	7.8	.05	2.16
	1921.			
	Jan. 15	8.8	.05	1.79
	Apr. 2	11.4	.03	1.98
	July 1	14.3	.05	2.36
	Oct. 1	17.3	.05	1.81
	1922.			
	Jan. 2	20.4	.05	1.88
	1920.			
FS-3 (25 pounds in paper-lined sugar barrel)	Apr. 20	.....	.06	2.01
	June 10	1.7	.08	2.30
	July 14	2.8	.05	3.12
	Aug. 14	3.8	.07	3.49
	Sept. 17	4.9	.09	3.81
	Oct. 15	5.8	.10	4.53
	Nov. 17	6.9	.15	5.32
	Dec. 15	7.8	.15	5.62
	1921.			
	Jan. 15	8.8	.25	5.70
	Apr. 2	11.4	.32	5.61
	July 1	14.3	.34	5.74
	Oct. 1	17.3	.32	5.68
	1922.			
	Jan. 2	20.4	.41	5.62
	1920.			
FS-4 (25 pounds in hardwood barrel)	Apr. 20	.....	.05	2.05
	June 10	1.7	.05	1.87
	July 14	2.8	.05	1.88
	Aug. 14	3.8	.07	2.00
	Sept. 17	4.9	.06	2.05
	Oct. 15	5.8	.05	2.04
	Nov. 17	6.9	.08	2.06
	Dec. 15	7.8	.05	2.94
	1921.			
	Jan. 15	8.8	.06	2.71
	Apr. 2	11.4	.09	2.38
	July 1	14.3	.05	2.72
	Oct. 1	17.3	.07	3.04
	1922.			
	Jan. 2	20.4	.07	3.38

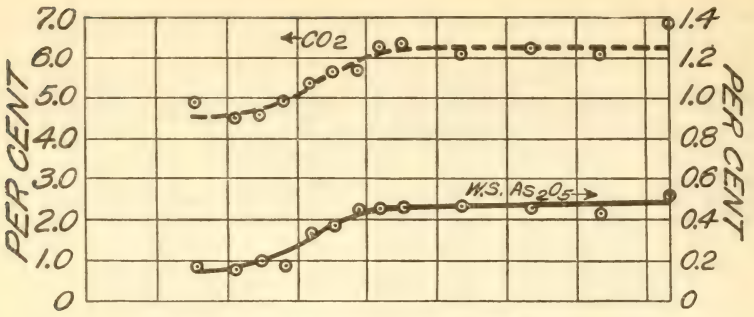

FIG. 25.—CS-5 (25 pounds in unlined veneer drum).

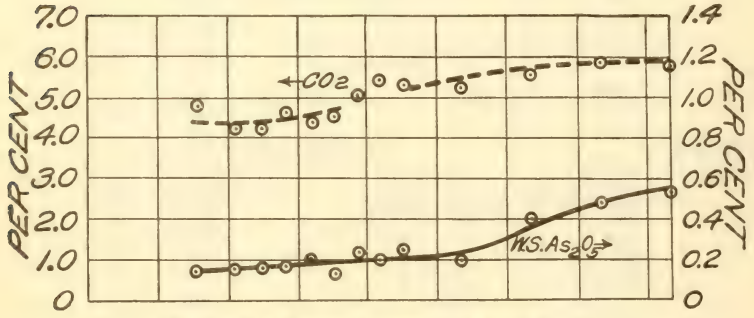

FIG. 26.—CS-6 (25 pounds in paper-lined veneer drum).

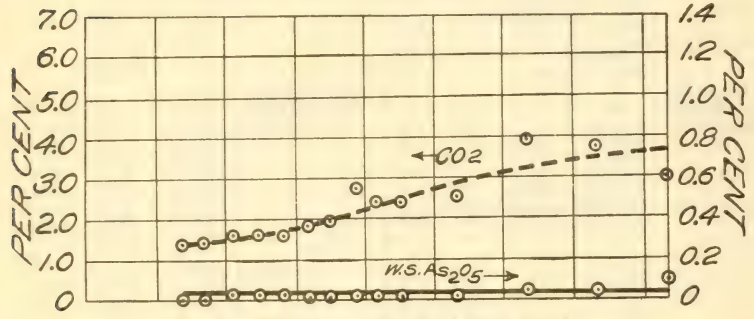

FIG. 27.—FT (100 pounds in unlined veneer drum).

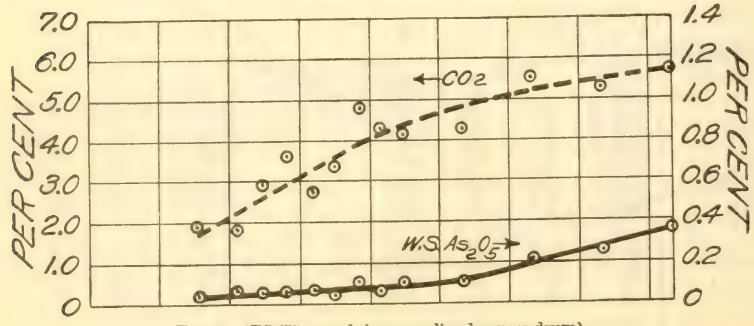

FIG. 28.—FS (75 pounds in paper-lined veneer drum).

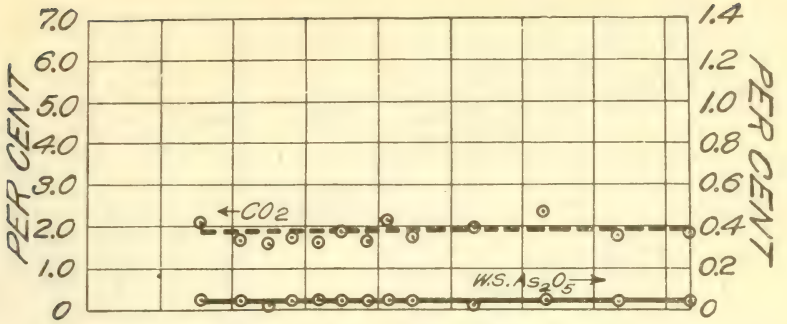

FIG. 29.—FS-1 (25 pounds in metal drum).

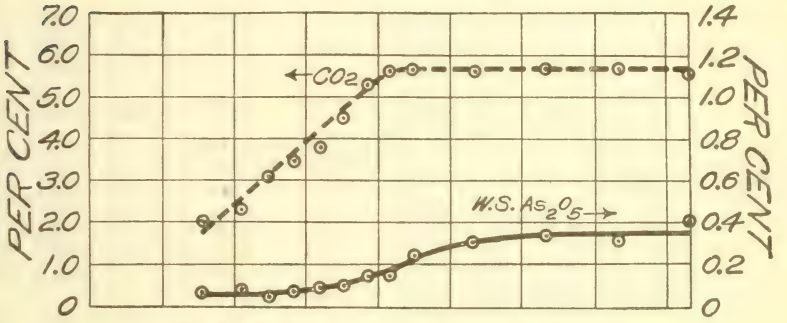

FIG. 30.—FS-3 (25 pounds in paper-lined sugar barrel).

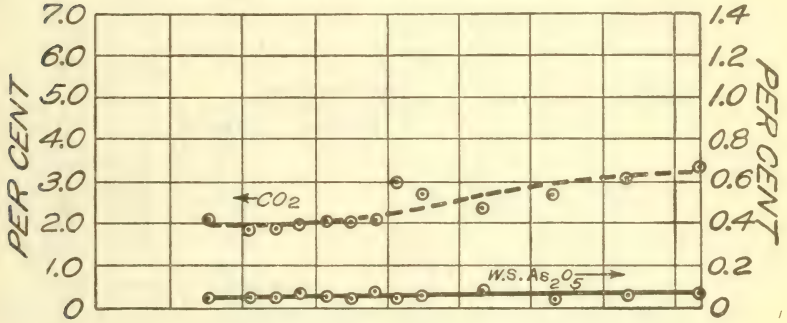

FIG. 31.—FS-4 (25 pounds in hardwood barrel).

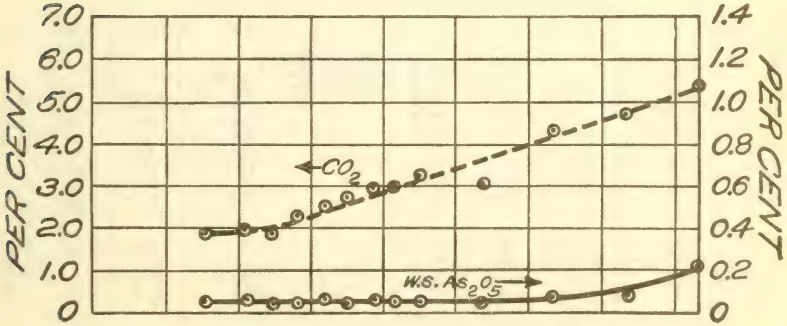

FIG. 32.—FS-5 (25 pounds in unlined veneer drum).

TABLE 2.—*Effect of storage on chemical composition of calcium arsenate*—Continued.

Sample examined.	Date sampled.	Period of storage	Water-soluble arsenic oxid (As_2O_5).	Carbon dioxid (CO_2).
FS-5 (25 pounds in unlined veneer drum)	1920.	*Mos.*	*Per ct.*	*Per ct.*
	Apr. 20	.....	0.05	1.90
	June 10	1.7	.06	1.96
	July 14	2.8	.05	1.88
	Aug. 14	3.8	.05	2.26
	Sept. 17	4.9	.06	2.53
	Oct. 15	5.8	.05	2.68
	Nov. 17	6.9	.07	2.95
	Dec. 15	7.8	.06	2.98
	1921.			
	Jan. 15	8.8	.06	3.28
	Apr. 2	11.4	.05	3.08
	July 1	14.3	.08	4.36
	Oct. 1	17.3	.09	4.77
	1922.			
	Jan. 2	20.4	.22	5.38
FS-6 (25 pounds in paper-lined veneer drum)	1920.			
	Apr. 20	.....	.06	1.93
	June 10	1.7	.05	2.16
	July 14	2.8	.05	2.34
	Aug. 14	3.8	.05	2.35
	Sept. 17	4.9	.06	2.30
	Oct. 15	5.8	.05	2.62
	Nov. 17	6.9	.07	3.48
	Dec. 15	7.8	.07	3.79
	1921.			
	Jan. 15	8.8	.07	4.06
	Apr. 2	11.4	.08	3.80
	July 1	14.3	.12	5.17
	Oct. 1	17.3	.33	5.51
	1922.			
	Jan. 2	20.4	.39	5.23
HW (50 pounds in hardwood barrel)	1920.			
	Apr. 12	.....	.11	.87
	June 23	2.4	.08	.90
	1921.			
	Jan. 14	9.1	.09	.93
	July 20	15.3	.07	1.07
	Nov. 25	19.4	.07	.97
	1922.			
	Mar. 1	22.6	.....	.....
HT (100 pounds in hardwood barrel)	1920.			
	Apr. 20	.....	.10	1.33
	May 4	.5	.07	.84
	June 10	1.7	.06	.86
	July 14	2.8	.04	.97
	Aug. 14	3.8	.02	.99
	Sept. 17	4.9	.02	.91
	Oct. 15	5.8	.02	1.25
	Nov. 17	6.9	.02	1.52
	Dec. 15	7.8	.02	2.35
	1921.			
	Jan. 15	8.8	.02	1.94
	Apr. 2	11.4	.02	2.92
	July 1	14.3	.05	2.87
	Oct. 1	17.3	.04	2.77
	1922.			
	Jan. 2	20.4	.12	3.72
HS (100 pounds in hardwood barrel)	1920.			
	Apr. 20	.....	0.10	1.07
	June 10	1.7	.05	.95
	July 14	2.8	.04	.88
	Aug. 14	3.8	.02	.98
	Sept. 17	4.9	.02	.85
	Oct. 15	5.8	.02	1.02
	Nov. 17	6.9	.02	1.04
	Dec. 15	7.8	.04	1.28
	1921.			
	Jan. 15	8.8	.02	.94
	Apr. 2	11.4	.02	1.48
	July 1	14.3	.02	1.54
	Oct. 1	17.3	.02	1.51
	1922.			
	Jan. 2	20.4	.07	1.69
HS-1 (25 pounds in metal drum)	1920.			
	Apr. 20	.....	.11	1.25
	June 10	1.7	.04	1.00
	July 14	2.8	.04	.97
	Aug. 14	3.8	.02	.92
	Sept. 17	4.9	.02	.93
	Oct. 15	5.8	.02	.95
	Nov. 17	6.9	.02	1.22
	Dec. 15	7.8	.02	1.18
	1921.			
	Jan. 15	8.8	.02	.98
	Apr. 2	11.4	.02	.97
	July 1	14.3	.02	.93
	Oct. 1	17.3	.02	1.01
	1922.			
	Jan. 2	20.4	.05	1.02
HS-4 (25 pounds in hardwood barrel)	1920.			
	Apr. 20	.....	.11	1.08
	June 10	1.7	.05	1.06
	July 14	2.8	.05	1.11
	Aug. 14	3.8	.05	1.20
	Sept. 17	4.9	.02	1.07
	Oct. 15	5.8	.02	1.06
	Nov. 17	6.9	.02	1.52
	Dec. 15	7.8	.02	1.66
	1921.			
	Jan. 15	8.8	.02	1.34
	Apr. 2	11.4	.02	1.38
	July 1	14.3	.02	2.52
	Oct. 1	17.3	.02	1.88
	1922.			
	Jan. 2	20.4	.07	1.81
HS-6 (25 pounds in paper-lined veneer drum)	1920.			
	Apr. 20	.....	.11	1.05
	June 10	1.7	.05	1.02
	July 14	2.8	.07	1.15
	Aug. 14	3.8	.05	1.10
	Sept. 17	4.9	.02	1.22
	Oct. 15	5.8	.05	1.28
	Nov. 17	6.9	.02	1.48
	Dec. 15	7.8	.02	2.24
	1921.			
	Jan. 15	8.8	.02	1.87
	Apr. 2	11.4	.02	1.78
	July 1	14.3	.04	2.56
	Oct. 1	17.3	.05	3.09
	1922.			
	Jan. 2	20.4	.07	3.15

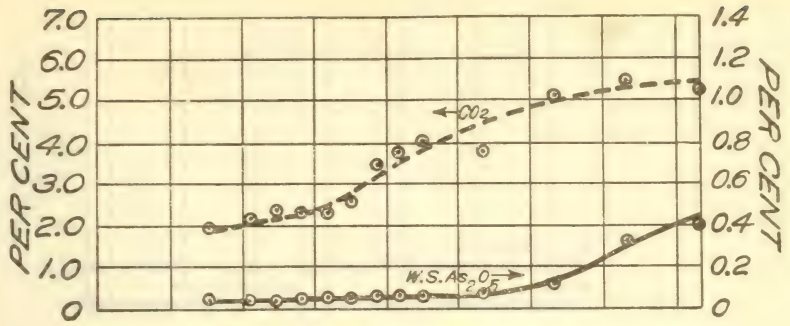

FIG. 33.—FS-6 (25 pounds in paper-lined veneer drum).

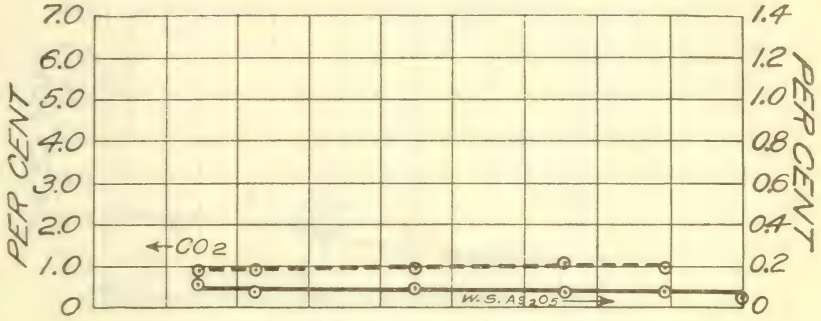

FIG. 34.—HW (50 pounds in hardwood barrel).

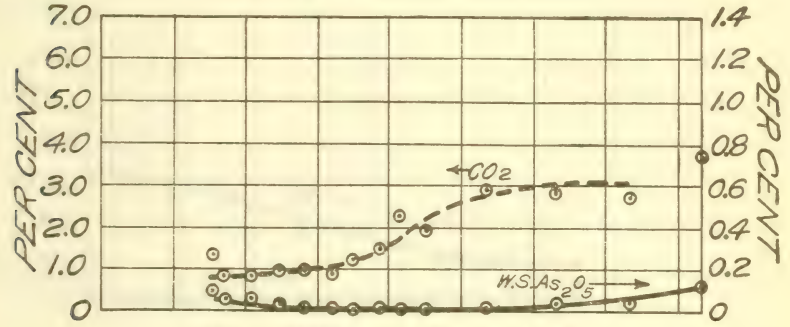

FIG. 35.—HT (100 pounds in hardwood barrel).

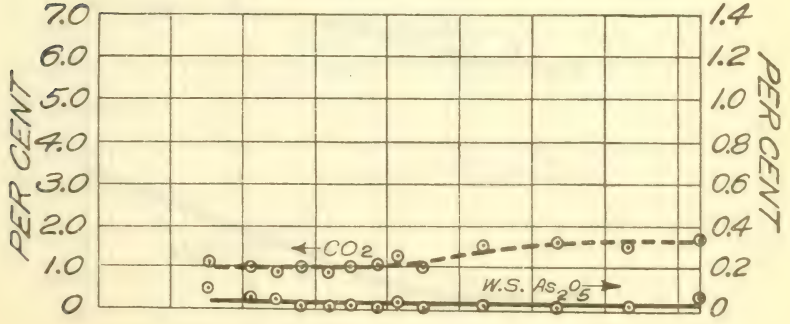

FIG. 36.—HS (100 pounds in hardwood barrel).

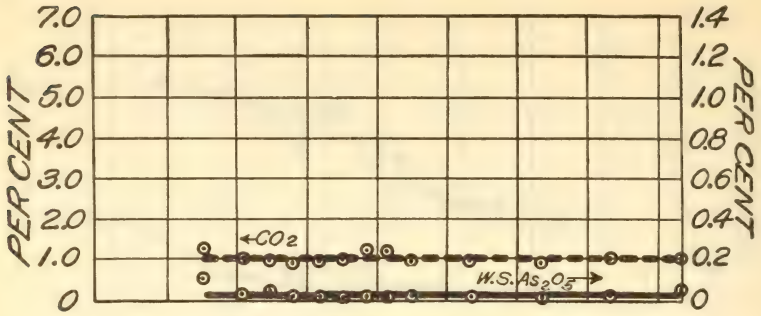

FIG. 37.—HS-1 (25 pounds in metal drum).

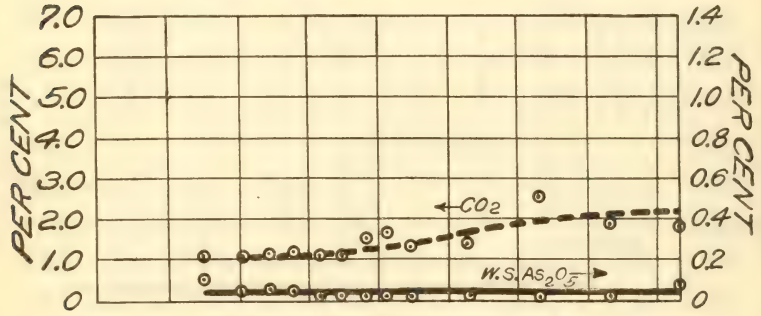

FIG. 38.—HS-4 (25 pounds in hardwood barrel).

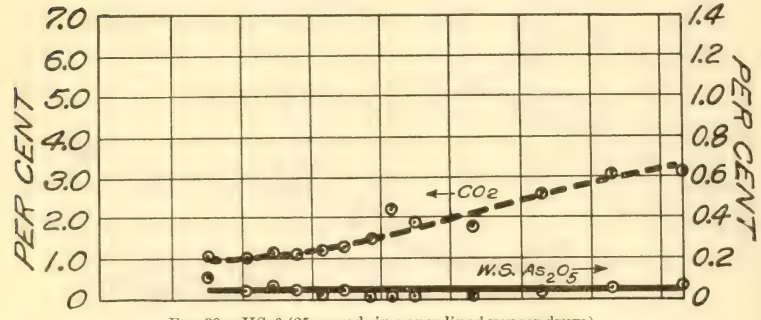

FIG. 39.—HS-6 (25 pounds in paper-lined veneer drum).

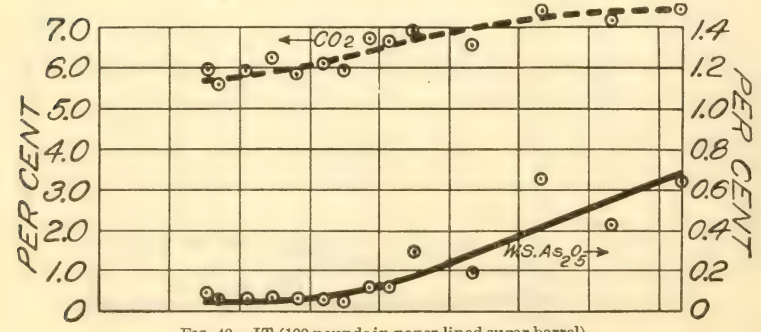

FIG. 40.—IT (100 pounds in paper-lined sugar barrel).

TABLE 2.—*Effect of storage on chemical composition of calcium arsenate*—Continued.

Sample examined.	Date sampled.	Period of storage.	Water-soluble arsenic oxid (As_2O_5).	Carbon dioxid (CO_2).
	1920.	*Mos.*	*Per ct.*	*Per ct.*
IT (100 pounds in paper-lined sugar barrel)...	Apr. 20	.....	0.08	5.95
	May 4	0.5	.07	5.61
	June 10	1.7	.06	5.92
	July 14	2.8	.07	6.25
	Aug. 14	3.8	.07	5.85
	Sept. 17	4.9	.06	6.08
	Oct. 15	5.8	.05	5.94
	Nov. 17	6.9	.12	6.76
	Dec. 15	7.8	.12	6.69
	1921.			
	Jan. 15	8.8	.28	6.90
	Apr. 2	11.4	.18	6.60
	July 1	14.3	.65	7.43
	Oct. 1	17.3	.42	7.18
	1922.			
	Jan. 2	20.4	.64	7.44
IS (100 pounds in paper-lined sugar barrel)...	1920.			
	Apr. 20	.....	.39	5.69
	June 10	1.7	.38	6.12
	July 14	2.8	.37	5.70
	Aug. 14	3.8	.50	5.79
	Sept. 17	4.9	.55	6.23
	Oct. 15	5.8	.69	6.08
	Nov. 17	6.9	.73	6.16
	Dec. 15	7.8	.68	6.39
	1921.			
	Jan. 15	8.8	.79	6.46
	Apr. 2	11.4	.77	6.49
	July 1	14.3	.85	6.26
	Oct. 1	17.3	.83	6.42
	1222.			
	Jan. 2	20.4	88	6.89
IS-1 (25 pounds in metal drum)	1920.			
	Apr. 20	.....	.36	6.09
	June 10	1.7	.35	6.06
	July 14	2.8	.32	5.58
	Aug. 14	3.8	.36	5.82
	Sept. 17	4.9	.43	5.85
	Oct. 15	5.8	.37	5.75
	Nov. 17	6.9	.37	5.86
	Dec. 15	7.8	.40	5.24
	1921.			
	Jan. 15	8.8	.36	6.00
	Apr. 2	11.4	.35	6.01
	July 1	14.3	.30	6.11
	Oct. 1	17.3	.36	6.03
	1922.			
	Jan. 2	20.4	.54	5.78
IS-3 (25 pounds in paper-lined sugar barrel)...	1920.			
	Apr. 20	.....	.31	5.51
	June 10	1.7	.54	6.09
	July 14	2.8	.77	6.58
	Aug. 14	3.8	.92	6.55
IS-3 (25 pounds in paper-lined sugar barrel)(con.).	Sept. 17	4.9	0.93	6.59
	Oct. 15	5.8	.93	6.20
	Nov. 17	6.9	.92	6.37
	Dec. 15	7.8	.96	6.61
	1921.			
	Jan. 15	8.8	.91	6.64
	Apr. 2	11.4	.88	6.46
	July 1	14.3	.90	6.41
	Oct. 1	17.3	.94	6.40
	1922.			
	Jan. 2	20.4	.94	7.10
IS-4 (25 pounds in hardwood barrel).....	1920.			
	Apr. 20	.....	.41	5.86
	June 10	1.7	.32	6.12
	July 14	2.8	.32	5.90
	Aug. 14	3.8	.39	5.83
	Sept. 17	4.9	.51	5.65
	Oct. 15	5.8	.49	5.71
	Nov. 17	6.9	.55	6.00
	Dec. 15	7.8	.71	5.98
	1921.			
	Jan. 15	8.8	.63	6.40
	Apr. 2	11.4	.70	6.23
	July 1	14.3	.78	6.27
	Oct. 1	17.3	.94	6.43
	1922.			
	Jan. 2	20.4	.94	6.30
IS-6 (25 pounds in paper-lined veneer drum)..	1920.			
	Apr. 20	.....	.37	5.74
	June 10	1.7	.42	6.36
	July 14	2.8	.62	6.11
	Aug. 14	3.8	.79	6.25
	Sept. 17	4.9	.97	6.45
	Oct. 15	5.8	.99	6.30
	Nov. 17	6.9	1.00	6.54
	Dec. 15	7.8	.96	6.64
	1921.			
	Jan. 15	8.8	.97	6.78
	Apr. 2	11.4	.92	6.32
	July 1	14.3	.90	6.42
	Oct. 1	17.3	.99	6.61
	1922.			
	Jan. 2	20.4	.97	6.27
JW (50 pounds in metal drum)	1920.			
	Apr. 12	.....	.30	2.69
	June 23	2.4	.24	2.90
	1921.			
	Jan. 14	9.1	.30	2.77
	July 20	15.3	.28	2.64
	Nov. 25	19.4	.26	2.76
	1922.			
	Mar. 1	22.6	.....	.....

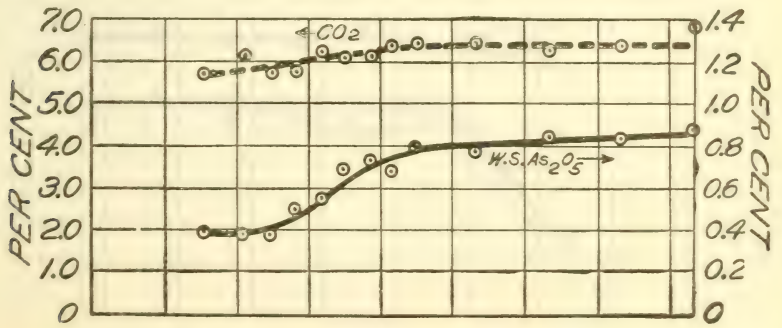

FIG. 41.—IS (100 pounds in paper-lined sugar barrel).

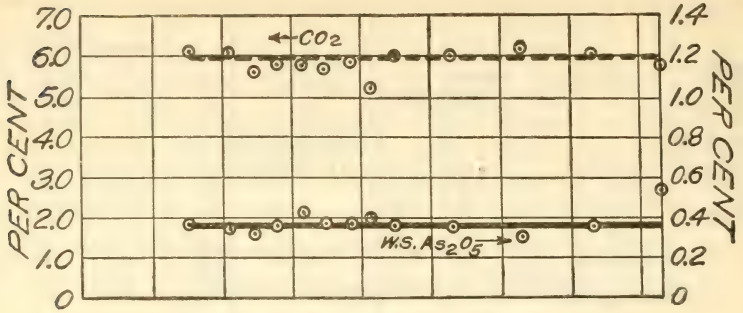

FIG. 42.—IS-1 (25 pounds in metal drum).

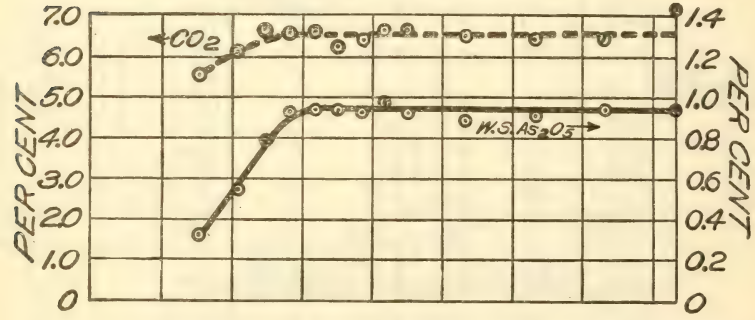

FIG. 43.—IS-3 (25 pounds in paper-lined sugar barrel).

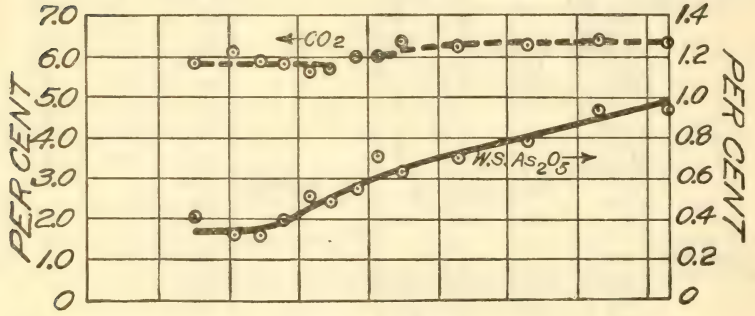

FIG. 44.—IS-4 (25 pounds in hardwood barrel).

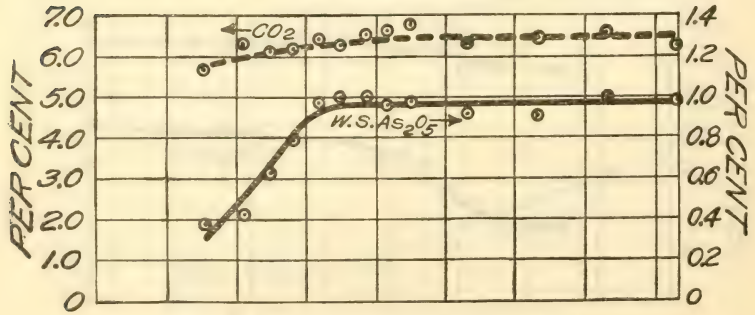

FIG. 45.—IS-6 (25 pounds in paper-lined veneer drum).

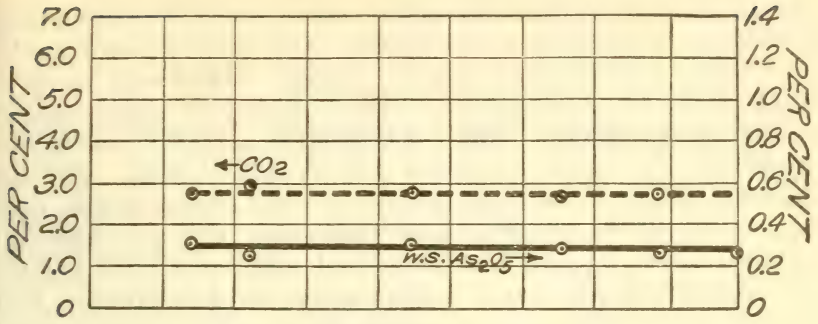

FIG. 46.—JW (50 pounds in metal drum).

DISCUSSION.

The arsenic oxid in water-soluble form and the carbon dioxid increased in all of the samples except those packed in the tightest containers. The close relationship between the increase in water-soluble arsenic and in carbon dioxid is plainly shown by the parallelism between the carbon dioxid and arsenic oxid curves for most of the samples.

In some cases the carbon dioxid content increases from the beginning, but the quantity of water-soluble arsenic oxid begins to increase only after some time has elapsed. This is undoubtedly due to the fact that a certain quantity of free lime is necessary to repress the "solubility" (really decomposition) of the calcium arsenate, and any free lime in excess of this amount can carbonate without affecting the soluble arsenic oxid. Once this limit is passed, however, decomposition begins. Many of the curves also show a limiting value for each of the two changes, these limits being reached at approximately the same time. This is well shown in the case of subsamples stored in sugar barrels, the most open containers, the greater number of which reached equilibrium in from six to nine months. It might naturally be assumed that this corresponds to the complete carbonation of the free lime in the samples, the final mixture being essentially tricalcium arsenate and calcium carbonate. Calculating the limiting carbon dioxid values to their equivalent calcium oxid values and subtracting these from the total calcium oxid, however, leaves calcium oxid remaining in amounts from 0.2 to 4.8 per cent in excess of the quantity necessary to form tricalcium arsenate with the total arsenic oxid of the sample. Pure tricalcium arsenate octahydrate [$Ca_3(AsO_4)_2.8H_2O$], containing 42 per cent total arsenic oxid, gave about 3 per cent water-soluble arsenic oxid, while the completely carbonated commercial samples exceeded 1 per cent in only one case (*B W*), which seems to argue against this being the only calcium arsenate in commercial samples. Further work will be necessary before the question of the presence of basic arsenates can be definitely settled.

There is a marked difference in the rate of change in the samples attributable to the types of containers. The samples stored in the metal drums showed practically no change. The change in those stored in the other containers varied from a very slight one, in the case of the tightest hardwood barrels, to a marked one in the case of the more open containers, such as sugar barrels. For the hardwood barrels the average increase in water-soluble arsenic oxid after 12 months was 0.06 per cent (maximum, 0.31 per cent) and in carbon dioxid, 0.85 per cent; at the end of 20 months, the average increase was 0.15 per cent in soluble arsenic oxid (maximum, 0.53 per cent) and 1.40 per cent in carbon dioxid. The samples stored in the paper-lined and unlined veneer drums showed little difference. At the end of 12 months the average increase in soluble arsenic oxid was 0.15 per cent (maximum, 0.55 per cent) and in carbon dioxid 1.38 per cent. After 20 months the average increase in soluble arsenic oxid was 0.30 per cent (maximum, 0.65 per cent) and in carbon dioxid 2.21 per cent. In the lined and unlined sugar barrels the average increase in soluble arsenic oxid after 12 months was 0.31 per cent (maximum, 0.57 per cent) and in carbon dioxid 1.72 per cent. After 20 months the soluble arsenic oxid increase averaged 0.45 per cent (maximum, 0.63 per cent) and the carbon dioxid increase averaged 2.01 per cent.

The average results showing the behavior of the material stored in the different containers are given in Table 3 and Figures 47, 48, 49, and 50. Each curve represents the average of the products of different manufacturers contained in packages of the same type. Four types of containers, metal drum (1), paper-lined sugar barrel (3), hardwood barrel (4), and paper-lined veneer drum (6), are represented under the six brands[8] included in the subdivision tests, and all of these (23 subdivisions) were subsampled on exactly the same dates. Each type of container is treated separately in order to bring out the parallelism between the carbon dioxid and water-soluble arsenic changes, and two graphs, showing all four curves for carbon dioxid and for arsenic oxid, respectively, are presented in Figures 51 and 52.

[8] Only five brands are represented in the case of the paper-lined barrels.

TABLE 3.—*Effect of type of container on chemical composition of calcium arsenate during storage.*

Type of container.	Date sampled.	Period of storage.	Water-soluble arsenic oxid (As_2O_5)	Carbon dioxid (CO_2).
	1920.	*Mos.*	*Per ct.*	*Per ct.*
Metal drums (samples AS-1, BS-1, CS-1, FS-1, HS-1, IS-1)	Apr. 20	.....	0.18	3.69
	June 10	1.7	.14	3.45
	July 14	2.8	.13	3.26
	Aug. 14	3.8	.13	3.39
	Sept. 17	4.9	.15	3.30
	Oct. 15	5.8	.13	3.33
	Nov. 17	6.9	.13	3.40
	Dec. 15	7.8	.14	3.38
	1921.			
	Jan. 15	8.8	.14	3.53
	Apr. 2	11.4	.14	3.45
	July 1	14.3	.13	3.54
	Oct. 1	17.3	.14	3.36
	1922.			
	Jan. 2	20.4	.16	3.33
Paper-lined sugar barrels (samples AS-3, BS-3, CS-3, FS-3, IS-3)	1920.			
	Apr. 20	.....	.18	4.00
	June 10	1.7	.26	4.41
	July 14	2.8	.32	4.77
	Aug. 14	3.8	.41	5.29
	Sept. 17	4.9	.47	5.50
	Oct. 15	5.8	.45	5.46
	Nov. 17	6.9	.50	6.09
	Dec. 15	7.8	.49	6.27
	1921.			
	Jan. 15	8.8	.52	6.27
	Apr. 2	11.4	.55	6.25
	July 1	14.3	.55	6.31
	Oct. 1	17.3	.55	6.34
	1922.			
	Jan. 2	20.4	.60	6.45
Hardwood barrels (samples AS-4, BS-4, CS-4, FS-4, HS-4, IS-4)	1920.	*Mos.*	*Per ct.*	*Per ct.*
	Apr. 20	.....	0.17	3.54
	June 10	1.7	.16	3.54
	July 14	2.8	.15	3.67
	Aug. 14	3.8	.17	3.91
	Sept. 17	4.9	.22	3.91
	Oct. 15	5.8	.23	4.06
	Nov. 17	6.9	.26	4.37
	Dec. 15	7.8	.29	4.51
	1921.			
	Jan. 15	8.8	.27	4.47
	Apr. 2	11.4	.31	4.49
	July 1	14.3	.32	4.86
	Oct. 1	17.3	.42	5.06
	1922.			
	Jan. 2	20.4	.46	5.09
Paper-lined veneer drums (samples AS-6, BS-6, CS-6, FS-6, HS-6, IS-6)	1920.			
	Apr. 20	.....	.16	3.53
	June 10	1.7	.16	3.56
	July 14	2.8	.20	3.56
	Aug. 14	3.8	.23	3.74
	Sept. 17	4.9	.28	3.81
	Oct. 15	5.8	.26	3.73
	Nov. 17	6.9	.29	4.29
	Dec. 15	7.8	.29	4.58
	1921.			
	Jan. 15	8.8	.32	4.60
	Apr. 2	11.4	.31	4.65
	July 1	14.3	.37	5.37
	Oct. 1	17.3	.45	5.51
	1922.			
	Jan. 2	20.4	.52	5.51

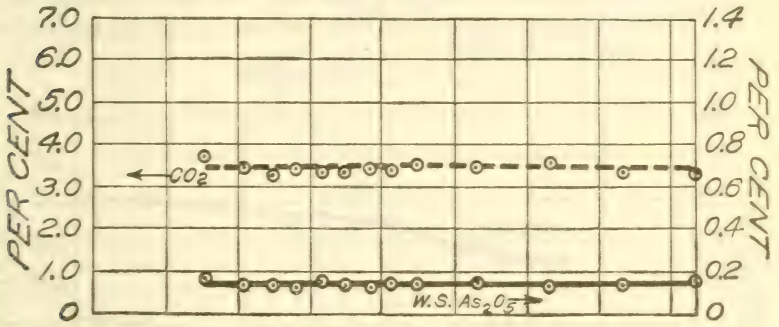

FIG. 47.—Average results with AS-1, BS-1, CS-1, FS-1, HS-1, IS-1 (metal drums).

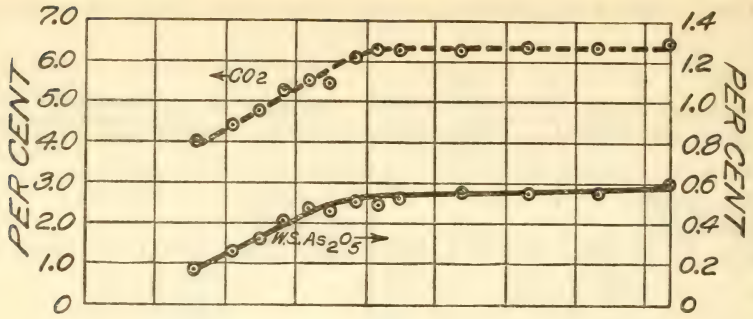

FIG. 48.—Average results with AS-3, BS-3, CS-3, FS-3, IS-3 (paper-lined sugar barrels).

All of the sugar barrels were in bad condition at the end of the test because of handling incident to sampling. The results of the tests show the unfitness of this type of container as a package for commercial purposes.

It is plainly shown that the containers are rated in the same order by both the carbon dioxid and the water-soluble arsenic oxid results. The metal drums show no change and the sugar barrels show the most rapid change, the other two being intermediate. Little difference between the lined and unlined containers of the same type is observed. The calcium arsenate stored in the sugar barrels apparently reached equilibrium in most cases in approximately eight months. No seasonal variation in the rate of change is apparent.

Very little information concerning the effect of locality was obtained. Strictly comparable results were possible only with samples *AW* and *AT*, and samples *HW* and *HT*. In both cases the rate of absorption of carbon dioxid was higher at Tallulah than at Washington. The authors are not in a position to state whether or not this was due to a higher carbon dioxid content in the air at Tallulah or to some other condition.

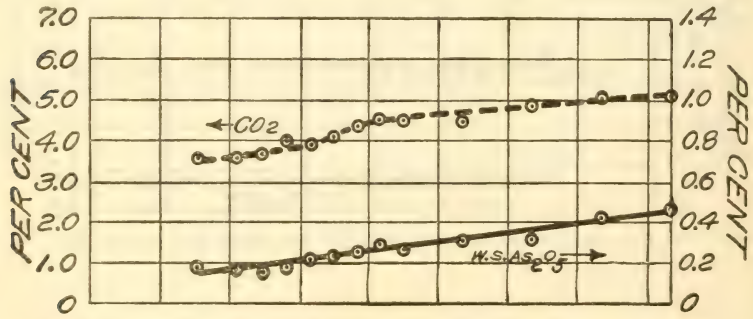

FIG. 49.—Average results with AS-4, BS-4, CS-4, FS-4, HS-4, IS-4 (hardwood barrels).

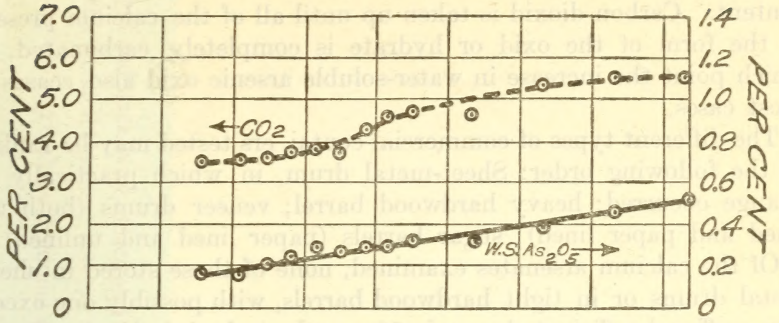

FIG. 50.—Average results with AS-6, BS-6, CS-6, FS-6, HS-6, IS-6 (paper-lined veneer drums).

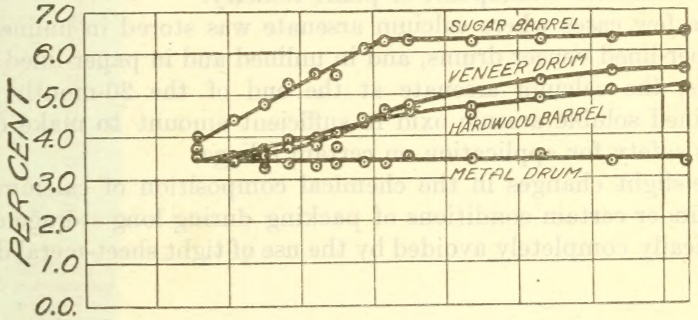

FIG. 51.—Effect of container on absorption of carbon dioxid.

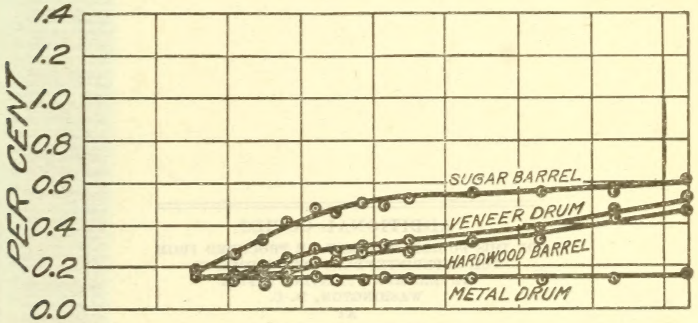

FIG. 52.—Effect of container on water-soluble arsenic oxid.

SUMMARY.

Commercial calcium arsenate in the dry powdered form manufactured for insecticidal purposes absorbs carbon dioxid slowly from the atmosphere during storage and increases in water-soluble arsenic-oxid content, unless it is packed in containers that are practically air-tight. The rates of these changes show a close relationship and depend largely upon the type of container in which the material is packed.

The absorption of carbon dioxid is the first change noted. This is followed a little later by a rise in the water-soluble arsenic oxid

content. Carbon dioxid is taken up until all of the calcium present in the form of the oxid or hydrate is completely carbonated, at which point the increase in water-soluble arsenic oxid also ceases in most cases.

The different types of commercial containers tested may be ranked in the following order: Sheet-metal drum, in which practically no change occurred; heavy hardwood barrel; veneer drums (both unlined and paper lined); sugar barrels (paper lined and unlined).

Of the calcium arsenates examined, none of those stored in sheet-metal drums or in tight hardwood barrels, with possibly one exception, suffered sufficient change in 20 months to be injuriously affected for use from the standpoint of plant toxicity.

In a few cases where calcium arsenate was stored in unlined and in paper-lined veneer drums, and in unlined and in paper-lined sugar barrels, the calcium arsenate at the end of the 20-month period contained soluble arsenic oxid in sufficient amount to make doubtful its safety for application on certain foliage.

The slight changes in the chemical composition of calcium arsenate under certain conditions of packing during long storage can be practically completely avoided by the use of tight sheet-metal drums.

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